UNITED STATES PATENT OFFICE.

LOUIS S. ROSS, OF NEWTONVILLE, MASSACHUSETTS, ASSIGNOR TO CENTRAL RAILWAY SIGNAL COMPANY, OF PITTSBURGH, PENNSYLVANIA, A CORPORATION OF NEW JERSEY.

TIME-BURNING RAILWAY SIGNAL-FUSEE.

1,094,596. Specification of Letters Patent. Patented Apr. 28, 1914.

No Drawing. Application filed June 27, 1912. Serial No. 706,231.

To all whom it may concern:

Be it known that I, LOUIS S. ROSS, a citizen of the United States, and a resident of Newtonville, in the county of Middlesex and State of Massachusetts, have invented an Improvement in Time-Burning Railway Signal-Fusees, of which the following description is a specification.

This invention relates to improvements in time burning railway signal fusees, the primary object thereof being to produce a fusee for such purpose that will not spontaneously ignite under conditions to which it is necessarily subjected, and which will not be extinguished when thrown from a moving train or otherwise subjected to severe shock, and which insures continuity of the flame after lighting.

In most compositions for railway signal fusees produced prior to my invention, there have been certain recognized characteristics of the ingredients contained in the fusees that render the latter extremely susceptible to spontaneous ignition, particularly in the presence of heat or moisture.

The railways of the United States for a number of years past have maintained a bureau for the safe transportation of explosives and other dangerous articles. This bureau employs chemists to investigate questions relating to the manufacture of explosives and other dangerous articles, and from time to time makes regulations and issues specifications prescribing the inherent characteristics of time burning railway signal fusees. These regulations must be passed upon and approved by the Interstate Commerce Commission to render them legally binding and effective. In accordance with the requirements of the said bureau, railway signal fusees comprise a paper tube of heavy, tough fiber, in which the composition is packed, carrying at one end a spike adapted to penetrate the railway ties or bed and having at its opposite end means for igniting the fusee. Railway signal fusees are usually thrown from the rear of a moving train and are necessarily therefore subjected to rough usage. It is therefore necessary to have the paper tube of sufficient strength to withstand this usage without breakage. These fusee paper tubes are therefore made of heavy, tough fiber, as stated, and the railroads require that the finished fusee must stand a specified, relatively heavy weight at its center when supported at its ends. One of the tests of the said bureau is that the fusee after burning a number of seconds in air must burn a specified time when completely submerged in water. It is further required by the said bureau that the fusee must burn a predetermined specified length of time. It must burn with brilliancy and force of flame and it must burn under either favorable or unfavorable weather conditions. In other words, the railway signal fusee must burn in strong winds or storms or even in pools of water or snowbanks.

By reason of the necessity of burning the tube in uniformity with the burning of the composition and also of the necessity that the composition burn with force and brilliancy, all successful compositions for railway signal fusees heretofore employed have contained sulfur and potassium chlorate as fundamental ingredients, with the single exception that a perchlorate, preferably perchlorate of potassium, has been substituted for the chlorate in a composition containing sulfur.

For many years it has been known that time burning railway signal fusees containing sulfur and potassium chlorate as heretofore combined were subject to spontaneous ignition and combustion due to climatic conditions of heat and moisture, because of the presence of said ingredients in the composition, and attempts have been made for many years by railway chemists and others to overcome this serious defect. Such spontaneous ignition has been attributed to the production by sulfur in the presence of heat and moisture of sulfurous and sulfuric acids, which in the presence of potassium chlorate decompose the latter and generate chlorin peroxid. The formation of sulfuric acid from sulfur requires the presence of oxygen, which is readily obtained in the breaking up of the potassium chlorate, whereby heat is generated, accelerating and helping to continue the reaction until a condition is reached that produces spontaneous combustion.

The so-called chlorate time burning rail-

way signal fusee is composed of chlorate, sulfur, carbohydrate and metallic nitrate in suitable proportions. In order to overcome the tendency to spontaneous ignition characteristic of the chlorate fusee, a so-called perchlorate fusee has been made by substituting perchlorate of potassium for the chlorate of potassium.

A fusee made of mixtures containing a perchlorate, such as perchlorate of potassium, is recognized to be harder to ignite and more easily extinguished when thrown from a moving train than a fusee of the so-called chlorate type. The so-called perchlorate fusee, in spite of this objection, is used because of its substantial freedom from spontaneous ignition.

Because of the fact that a perchlorate fusee is substantially free from danger of spontaneous ignition, I have conducted a series of experiments in order to produce if possible a perchlorate fusee that will not be readily extinguished by sudden shock and the flame of which will burn with continuity. I have as the result of said experiments discovered that if in addition to a suitable quantity of potassium or any other suitable perchlorate, such, for example, as barium, sodium or ammonium perchlorate, I employ a small proportion of a suitable chlorate, such, for example, as chlorate of potassium, of barium, of sodium, of ammonium or any other suitable chlorate, I not only produce a time burning railway signal fusee which is not liable to spontaneous ignition, but I obtain a fusee, the temperature of ignition of which is maintained at the desired high point of 250° C. or higher. In addition, I increase the inflammability of the fusee compound and increase the tenacity and force of the flame of the fusee composition. This fusee is not readily extinguished under adverse conditions. Moreover the stability of the perchlorate (by reason of the employment of which the so-called perchlorate fusee is readily extinguished when thrown from a train or upon receiving a sudden shock) is modified by the chlorate, so that the modified fusee is not easily extinguished by sudden shock or when thrown from a train.

In my tests and experiments to eliminate the known objections of the perchlorate fusee and to perfect such fusee, I have ascertained that the employment of a carbohydrate in a perchlorate fusee is gravely and peculiarly objectionable. That is to say, I have ascertained that although a carbohydrate may be employed satisfactorily in a so-called chlorate fusee, its presence in a perchlorate fusee is objectionable owing to the combined presence of carbohydrate and perchlorate. A serious objection to the so-called perchlorate fusee is due to the increased oxidizing power of perchlorate which differs from chlorate only in that it contains an added atom of oxygen. This objection is a particularly serious one in the use of fusees of combined colors, for the tendency to incandescence and excessive brilliancy causes the red, yellow and green fusee flames to lose their characteristic colors and gradually to merge nearer a whiter light. I have discovered in the course of long experimentation that this objection is very materially overcome by the elimination of carbohydrate and by the employment of hydrocarbon or carbon, or both, or in other words, by the employment of carbonaceous material that is devoid of oxygen. The overcoming of the said objection I attribute largely to the fact that the carbohydrate contains oxygen, which is not present in the hydrocarbon or in the carbon. The added oxygen present in the perchlorate is to a very considerable extent compensated for by the absence thereof in the hydrocarbon and carbon, even though the amount of hydrocarbon or carbon, or both, is less than that of the perchlorate. A further objection to the so-called perchlorate fusee is that it burns too quickly; that is, with a decreased burning interval after a short period following manufacturing. As a result of my said experiments, I attribute this defect in part at least to the added oxygen present in the perchlorate. The absence of oxygen in the hydrocarbon and in the carbon compensates therefor, and hence there is less tendency of my fusee to burn for a shorter period than the minimum time limit. The so-called perchlorate fusee is also objectionable in that it requires a temperature of substantially 310° C. to ignite, this being considerably higher than the 250° C. required by the bureau for the safe transportation of explosives. I have discovered that by eliminating carbohydrate and by employing hydrocarbon or carbon, or both, substantially as herein set forth, I am enabled to make a fusee containing perchlorate, which fusee is somewhat more readily inflammable than the perchlorate-carbohydrate fusee.

Not only does the carbohydrate heretofore employed in the manufacture of perchlorate fusees leave an objectionable residue and also prevent the proper burning of the perchlorate fusee, but the carbohydrate has been objected to by engineers of tests and chemists upon the ground that certain forms thereof, such as sawdust, constitutes an adulterant, the presence whereof in the fusee composition is readily shown by subjecting the composition to the action of gasolene. Moreover, the addition of the carbohydrate in the form of sawdust, starch, flour, etc., not only has the objections heretofore pointed out, but such addition makes the fusee more bulky and hence of increased length for a predetermined burning time, thus rendering

it more liable to breakage when it is thrown from a train in use.

The so-called perchlorate fusee is also objectionable in that it is more easily extinguished when thrown from a moving train than a fusee of the so-called chlorate type, and it is harder to ignite than a fusee of the said chlorate type. In my experiments as heretofore set forth, I have eliminated the carbohydrate and have employed carbonaceous material that is devoid of oxygen and preferably either in the form of a hydrocarbon or of a carbon, or of both. In making such elimination and in employing hydrocarbon or carbon, or both, to the exclusion of a carbohydrate, I have been compelled to make many tests under commercial conditions before obtaining a perchlorate fusee wherein such carbonaceous material is present in the proper proportions with respect to the other ingredients, namely, the perchlorate, the sulfur and the metallic salt or metallic nitrate. I have, however, secured satisfactory results with the elimination of the carbohydrate and by the employment of a hydrocarbon or of a carbon or both; that is, of a carbonaceous material devoid of oxygen. Moreover, I have found that a perchlorate fusee containing such carbonaceous material devoid of oxygen is not so readily extinguished as is a perchlorate fusee containing carbohydrate, and that it is not so hard to ignite as is a perchlorate fusee containing carbohydrate. In other words, I have not only, in the elimination of the carbohydrate, eliminated certain objections which my experiments have convinced me were due to the carbohydrate, but I have eliminated certain objections heretofore supposed to be inherently and necessarily characteristic of a perchlorate fusee, and due solely to the presence of the perchlorate; namely, the relative ease with which it is extinguished when thrown from a moving train, the relative difficulty of igniting the same, the tendency of the flames toward incandescence, and the high temperature required for ignition. I have furthermore discovered that by using hydrocarbon or carbon, or both, the perchlorate fusee when properly made will not only not be so easily extinguished when thrown and will not be so hard to ignite, but it will burn with the production of proper colors.

Perchlorate fusees as heretofore manufactured usually contain from five or six to twenty per cent. of potassium or other perchlorate combined with which are nitrate, sulfur and carbohydrate with charcoal and antimony if desired, in substantially the following proportions: nitrate 50 to 95%, sulfur 3 to 23%, carbohydrate 1 to 11%, charcoal 1%, antimony (sulfid) 1%.

In accordance with my invention I provide as customary in the so-called perchlorate fusee a suitable mixture of perchlorate (preferably perchlorate of potassium, though I may employ any suitable perchlorate, such for example, barium, sodium or ammonium perchlorate) sulfur, hydrocarbon, or any suitable carbonaceous material devoid of oxygen, and a metallic salt, such as a metallic nitrate or oxid to which, if desired, I may add charcoal and antimony. The perchlorate of potassium is used to furnish the principal supply of oxygen, the sulfur mainly to increase combustion, the hydrocarbon and the carbonaceous material to furnish carbon and hydrogen, to aid combustion and to smooth and deepen the flame, and the metallic salt, preferably that of strontium, barium or sodium, to constitute the base or color ingredients.

While the proportions of these ingredients may be varied, they may be those previously stated with the admixture of a suitable quantity of chlorate of potassium, of barium, of sodium, of ammonium or any other suitable chlorate in a small quantity, preferably not exceeding five per cent. of the entire mixture. The carbonaceous material preferably employed by me consists of red gum (the powdered bark of the red gum—*Eucalyptus rostrata*), charcoal and grease, such as paraffin and naphthalene in suitable proportions. It will be understood that I may employ one or more hydrocarbons or carbons, either alone or in suitable mixture, or that any two of such carbonaceous materials may be employed. The carbonaceous materials employed, and which are preferably carbons or hydrocarbons, are devoid of oxygen.

I have obtained excellent results by employing the following formulæ, wherein the ingredients are specified first in parts by weight and then in percentages:

	Parts by weight.	*Percentage.*
Metallic nitrate	144	70.24
Sulfur	20	9.75
Carbon—preferably charcoal	2½	1.70
Hydrocarbon—preferably naphthalene or paraffin	12	5.85
Potassium perchlorate	21	10.24
Potassium chlorate	4½	2.19
Metallic nitrate	140	68.96
Sulfur	20	9.85
Carbon—preferably charcoal	1½	0.73
Hydrocarbon—preferably naphthalene or paraffin	11½	5.66
Potassium percholate	25½	12.56
Potassium chlorate	4½	2.21
Metallic nitrate	154	74.75
Sulfur	22¾	11.00
Carbon	4⅓	2.10
Hydrocarbon	12¼	5.94
Potassium perchlorate	9	4.37
Potassium chlorate	3¾	1.80

I have secured excellent results by employing substantially 68 to 76% metallic nitrate; substantially 9 to 12% sulfur; substantially 6 to 8% carbonaceous material; substantially 4 to 13% potassium perchlorate and substantially 1½ to 3⅓% potassium chlorate.

As previously stated, the proportion or quantity of chlorate employed is a small one and for best results should not exceed 5% of the entire composition. Excellent results have been obtained by using about 2%, as appears from the above formulæ. Preferably I employ potassium chlorate in a red fusee and a barium chlorate in a green fusee, but by using any chlorate I have succeeded in making a railway time burning signal fusee having practically all the advantages of the chlorate fusee, and one in which the ease of extinguishment characteristic of the perchlorate fusee is greatly lessened, and in many cases is wholly or substantially wholly overcome.

Experiments carried out by me and extending over a period of a number of months have shown that a fusee constructed as herein disclosed will successfully meet the high temperature of ignition test prescribed by the bureau for the safe transportation of explosives. Moreover such fusee is found to be immune from spontaneous ignition, though heretofore it had been supposed that a time burning railway signal fusee containing any material proportion of chlorate of potassium or other chlorate was liable to spontaneous ignition. In other words, it had been heretofore supposed that any fusee containing more than a trace of chlorate was liable to spontaneous ignition when subjected to moisture and an elevated temperature. After an extended series of experiments, I have, however, as above set forth, demonstrated that a time burning railway signal fusee may contain a relatively small proportion of chlorate, preferably about two, two and a half or three per cent. of a suitable chlorate, and is not liable to spontaneous ignition, provided it contains a suitable proportion of a perchlorate, such, for example, as one of the perchlorates previously referred to by me. It will be observed that in the several formulæ above set forth, the quantity or proportion of perchlorate exceeds that of chlorate, and with such relative proportions I have obtained the best results.

The time burning railway signal fusee compound embodying my invention contains as essential ingredients a perchlorate and a chlorate (any suitable perchlorate and any suitable chlorate being used) together with sulfur. To this composition I add one or more of the other ingredients specified by me, and for the best results I add metallic nitrate and some suitable carbonaceous material.

I employ the term "carbonaceous material" to include hydrocarbons, carbons or other suitable carbon-containing material devoid of oxygen.

Having thus described one embodiment of my invention I desire it to be understood that although specific terms are employed, they are used in a generic and descriptive sense and not for purposes of limitation, the scope of the invention being set forth in the following claims.

Claims:

1. A time burning railway signal fusee comprising a metallic nitrate, carbonaceous material, devoid of oxygen, sulfur, perchlorate, and a small quantity of chlorate not exceeding substantially five per cent. of the entire composition, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

2. A time burning railway signal fusee including sulfur, perchlorate, carbonaceous material devoid of oxygen and a small quantity of chlorate not exceeding substantially five per cent. of the entire composition, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

3. A time burning railway signal fusee comprising a metallic nitrate, carbonaceous material devoid of oxygen, sulfur, perchlorate of potassium, and a small quantity of chlorate of potassium not exceeding substantially five per cent. of the entire composition, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

4. A time burning railway signal fusee comprising a metallic nitrate, carbonaceous material devoid of oxygen, sulfur, perchlorate, and a quantity of chlorate less than the said perchlorate, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

5. A time burning railway signal fusee comprising a metallic nitrate, sulfur, hydrocarbon, carbon, perchlorate of potassium, and a small quantity of chlorate of potassium not exceeding substantially five per cent. of the entire composition, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

6. A time burning railway signal fusee comprising about seventy per cent. metallic nitrate, about ten per cent. sulfur, about seven per cent. carbonaceous material devoid of oxygen and also containing perchlorate and chlorate, the quantity of chlorate being less than the quantity of perchlorate, thereby producing a time burning, railway signal fusee compound burning with bril-

liancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

7. A time burning railway signal fusee comprising about seventy per cent. metallic nitrate, about ten per cent. sulfur, about seven per cent. carbonaceous material devoid of oxygen, about ten per cent. perchlorate and about two per cent. chlorate, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

8. A time burning railway signal fusee comprising about seventy per cent. metallic nitrate, about ten per cent. sulfur, about seven per cent. carbonaceous material devoid of oxygen, about ten per cent. perchlorate of potassium and about two per cent. chlorate of potassium, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

9. A time burning railway signal fusee comprising a metallic nitrate, carbonaceous material devoid of oxygen, sulfur, perchlorate, and a small quantity of chlorate insufficient when combined with the perchlorate in the specified composition to render the fusee liable to spontaneous ignition, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame, and not liable to spontaneous ignition or combustion.

10. A time burning railway signal fusee comprising substantially sixty-eight to seventy-six per cent. metallic nitrate, substantially nine to twelve per cent. sulfur, substantially six to eight per cent. carbonaceous material devoid of oxygen, substantially four to thirteen per cent. potassium perchlorate, and substantially one and a half to three and a half per cent. potassium chlorate, thereby producing a time burning, railway signal fusee compound burning with brilliancy, tenacity and force of flame and not liable to spontaneous ignition or combustion.

In testimony whereof, I have signed my name to this specification, in the presence of two subscribing witnesses.

LOUIS S. ROSS.

Witnesses:
IRVING U. TOWNSEND,
EVERETT S. EMERY.